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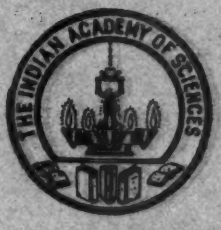

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POTENTIAL CONSTANTS OF ETHYLENE OXIDE, ETHYLENE OXIDE-d_4 AND ETHYLENE SULPHIDE

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1. Introduction

The possible structure of ethylene oxide (C_2H_4O) molecule[1] is that the O and the two C atoms form an isosceles triangle and the two CH_2 groups form planes at right angles to the C_2O plane. Under this assumption, the molecule belongs to the point group C_{2v} and the number of fundamental frequencies is fifteen. Of these fifteen fundamentals, five are of A_1 type, three of A_2 type, four of B_1 type and three of B_2 type. The fundamentals of the A_2 species are inactive in infra-red but active in Raman effect. The fundamentals of the other three species are active in both infra-red and Raman spectra.

The vibrational spectrum of ethylene oxide has been measured by a number of authors. Lord and Nolin[2] have studied the infra-red and Raman spectra of ethylene oxide and also of its deuterium analogue and have made an assignment of the observed fundamentals. Their assignment correlates well with that of the analogous molecules, cyclopropane and cyclopropane-d_4.

Gunthard *et al.*[3] have calculated three force constants of ethylene oxide molecule by assuming a simple valence force field and making use only of the A_2 and B_2 type frequencies. Stone[4] has used a generalised valence force field and has evaluated ten force constants taking into account the assignment of the fundamentals given earlier by Linnett[5] and by Herzberg.[1] In the present investigation a more general potential function involving all possible force constants has been used. The method adopted for the evaluation of the force constants is the Wilson's F-G matrix method[6] making use of symmetry co-ordinates. The latest assignment of frequencies given by Lord and Nolin has been followed. Evaluation of force constants in the case of the deuterium analogue of ethylene oxide has also been made making use of the frequencies given by Lord and Nolin. The molecular parameters have been taken from Cunningham *et al.*[7]

Ethylene sulphide molecule possesses the same structure as ethylene oxide. The vibrational spectrum of this molecule has been studied by Thompson and Dupre.[8] The procedure adopted for the evaluation of force constants of ethylene oxide has been extended to the case of ethylene sulphide also.

2. SYMMETRY CO-ORDINATES

The internal co-ordinates that are used in the construction of the symmetry co-ordinates are the changes in the bond distances d_1, d_2, d_3, d_4, D, r_1, r_2 and the changes in the interbond angles α_1, α_2, η_1, η_2, θ, β_1, β_2, β_3, β_4, ϕ_1, ϕ_2, ϕ_3, ϕ_4 (Fig. 1).

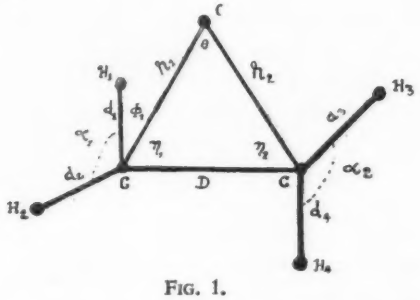

FIG. 1.

The orthonormalised set of symmetry co-ordinates, satisfying transformation conditions, is constructed as given below:

For the A_1 type,

$$R_1 = \Delta D$$
$$R_2 = (\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)/2$$
$$R_3 = (\Delta \alpha_1 + \Delta \alpha_2)/\sqrt{2}$$
$$R_4 = (\Delta r_1 + \Delta r_2)/\sqrt{2}$$
$$R_5 = \Delta \theta$$

For the A_2 type,

$$R_6 = (\Delta d_1 - \Delta d_2 - \Delta d_3 + \Delta d_4)/2$$
$$R_7 = (\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 + \Delta \beta_4)/2$$
$$R_8 = (\Delta \phi_1 - \Delta \phi_2 - \Delta \phi_3 + \Delta \phi_4)/2$$

For the B_1 type,

$$R_9 = (\Delta r_1 - \Delta r_2)\sqrt{2}$$
$$R_{10} = (\Delta \alpha_1 - \Delta \alpha_2)/\sqrt{2}$$

$$R_{11} = (\Delta\eta_1 - \Delta\eta_2)/\sqrt{2}$$

$$R_{12} = (\Delta d_1 + d_2 - \Delta d_3 - \Delta d_4)/2$$

For the B_2 type,

$$R_{13} = (\Delta d_1 - \Delta d_2 + \Delta d_3 - \Delta d_4)/2$$

$$R_{14} = (\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)/2$$

$$R_{15} = (\Delta\phi_1 - \Delta\phi_2 + \Delta\phi_3 - \Delta\phi_4)/2$$

3. F Matrix

The general potential function used here involves the force constants f_D, f_d, f_r, f_α, f_β, f_ϕ, f_η, f_θ, f_{dd}, f_{rr}, f_{Dd}, f_{Dr}, $f_{d\phi}$, f_{dr}, $f_{d\alpha}$, $f_{d\beta}$, $f_{r\theta}$, $f_{r\eta}$, $f_{\alpha\beta}$, $f_{\beta\beta}$, and $f_{\phi\phi}$. The elements of the potential energy matrix, using the above potential function and the U and U′ matrices, formed from the coefficients of the internal co-ordinates in the symmetry co-ordinates, are given below for the different vibrational species:—

For the A_1 type:

$$\begin{vmatrix} F_{11} & F_{12} & F_{13} & F_{14} & F_{15} \\ F_{21} & F_{22} & F_{23} & F_{24} & F_{25} \\ F_{31} & F_{32} & F_{33} & F_{34} & F_{35} \\ F_{41} & F_{42} & F_{43} & F_{44} & F_{45} \\ F_{51} & F_{52} & F_{53} & F_{54} & F_{55} \end{vmatrix} = \begin{vmatrix} f_D & 2f_{Dd} & 0 & \sqrt{2}f_{Dr} & 0 \\ 2f_{Dd} & f_d + f_{dd} & \sqrt{2}df_{d\alpha} & \sqrt{2}f_{dr} & 0 \\ 0 & \sqrt{2}df_{d\alpha} & d^2f_\alpha & 0 & 0 \\ \sqrt{2}f_{Dr} & \sqrt{2}f_{dr} & 0 & f_r + f_{rr} & \sqrt{2}rf_{r\theta} \\ 0 & 0 & 0 & \sqrt{2}rf_{r\theta} & r^2f_\theta \end{vmatrix}$$

For the A_2 and B_2 types the elements are the same:

$$\begin{bmatrix} F_{66} & F_{67} & F_{68} \\ F_{76} & F_{77} & F_{78} \\ F_{86} & F_{87} & F_{88} \end{bmatrix} = \begin{bmatrix} F_{1313} & F_{1314} & F_{1315} \\ F_{1413} & F_{1414} & F_{1415} \\ F_{1513} & F_{1514} & F_{1515} \end{bmatrix} = \begin{bmatrix} f_d - f_{dd} & df_{d\beta} & df_{d\phi} \\ df_{d\beta} & d^2(f_\beta - f_{\beta\beta}) & 0 \\ df_{d\phi} & 0 & r^2(f_\phi - f_{\phi\phi}) \end{bmatrix}$$

For the B_1 type:

$$\begin{bmatrix} F_{99} & F_{910} & F_{911} & F_{912} \\ F_{109} & F_{1010} & F_{1011} & F_{1012} \\ F_{119} & F_{1110} & F_{1111} & F_{1112} \\ F_{129} & F_{1210} & F_{1211} & F_{1212} \end{bmatrix} = \begin{bmatrix} (f_r - f_{rr}) & 0 & 0 & \sqrt{2}f_{dr} \\ 0 & d^2f_\alpha & 0 & \sqrt{2}df_{d\alpha} \\ 0 & 0 & r^2f_\eta & 0 \\ \sqrt{2}f_{dr} & \sqrt{2}df_{d\alpha} & 0 & (f_d + f_{dd}) \end{bmatrix}$$

4. G MATRIX

The elements of the kinetic energy matrix corresponding to the different species are obtained following the methods outlined by Wilson and are given below:—

For the A_1 type:

$$G_{11} = 2\mu_C$$

$$G_{22} = \mu_H + \mu_C (1 + \cos \alpha)$$

$$G_{33} = 2 \{\mu_H + \mu_C (1 - \cos \alpha)\}/d^2$$

$$G_{44} = \mu_C + \mu_0 (1 + \cos \theta)$$

$$G_{55} = 2 \{\mu_C + \mu_0 (1 - \cos \theta)\}/r^2$$

$$G_{12} = 2\mu_C \cos \beta$$

$$G_{13} = -2\sqrt{2}\mu_C \cos \beta (1 - \cos \alpha)/d \sin \alpha$$

$$G_{14} = \sqrt{2}\mu_C \cos \eta$$

$$G_{15} = 2\mu_C \cos \eta (\cos \theta - 1)/r \sin \theta$$

$$G_{23} = -\sqrt{2}\mu_C \sin \alpha/d$$

$$G_{24} = \sqrt{2}\mu_C \cos \phi$$

$$G_{25} = 2\mu_C (\cos \phi \cos \theta + \cos \phi)/r \sin \theta$$

$$G_{34} = -2\mu_C \cos \phi (1 - \cos \alpha)/d \sin \alpha$$

$$G_{35} = -2\sqrt{2}\mu_C (1 - \cos \alpha)(\cos \phi \cos \theta + \cos \phi)/rd \sin \alpha \sin \theta$$

$$G_{45} = -\sqrt{2}\mu_0 \sin \theta/r$$

For the A_2 type:

$$G_{66} = \mu_H + \mu_C (1 - \cos \alpha)$$

$$G_{77} = \mu_H/d^2 + \mu_C [(1 - \cos \alpha) \{1 + D^2 (1/D - \cos \beta/d)^2\} + 2D (1/D - \cos \beta/d)(1 + \cos x)]/D^2 \sin^2 \beta$$

$$G_{88} = \mu_H/d^2 + \mu_C (1/r - \cos \phi/d)^2 (1 - \cos \alpha)/\sin^2 \phi + \mu_0 \{(1 - \cos \alpha) - (1 + \cos x)\}/r^2 \sin^2 \phi$$

$$G_{67} = -\mu_C \{(1/D - \cos \beta/d)(1 - \cos \alpha)/\sin \beta + (1 + \cos x)/D \sin \beta\}$$

$$G_{68} = -\mu_C (1/r - \cos \phi/d)(1 - \cos \alpha)/\sin \phi$$

$$G_{78} = \mu_H (\cos\eta - \cos\beta\cos\phi)/d^2 \sin\phi \sin\beta + \mu_c (1/r - \cos\phi/d)\,[(1/D - \cos\beta/d)(1 - \cos\alpha) + (1 + \cos x)/D]/\sin\phi \sin\beta$$

where $x = 2\beta - 180$;

For the B_1 type:

$$G_{99} = \mu_c + \mu_0 (1 - \cos\theta)$$

$$G_{1010} = 2\{\mu_H + \mu_c (1 - \cos\alpha)\}/d^2$$

$$G_{1111} = \mu_c [(1/D - \cos\eta/r)^2 + (1/r - \cos\eta/D)^2 + 2\cos\eta\,(1/D - \cos\eta/r)(1/r - \cos\eta/D) + (1 + 3\cos^2\eta)/D^2 + 2/D\,\{1/D - \cos\eta/r)(\cos^2\eta + \cos\theta) + 2\cos\eta\,(1/r - \cos\eta/D)\}/\sin^2\eta + \mu_0\{(1 - \cos\theta)\cos^2\eta + 2\}/r^2\sin^2\eta$$

$$G_{1212} = \mu_H + \mu_c (1 + \cos\alpha)$$

$$G_{910} = -2\mu_c \cos\phi\,(1 - \cos\alpha)/d\sin\alpha$$

$$G_{911} = -\mu_c [\{(1/D - \cos\eta/r) + \cos\eta\,(1/r - \cos\eta/D)\} + (\cos^2\eta + \cos\theta)/D] + \mu_0 \cos\eta\,(1 - \cos\theta)/r\sin\eta$$

$$G_{912} = \sqrt{2}\mu_c \cos\phi$$

$$G_{1011} = 2\mu_c (1 - \cos\alpha)\,[(1/D - \cos\eta/r)\cos\phi + (1/r - \cos\eta/D) \times \cos\beta + (\cos\beta\cos\eta - \cos\phi)/D]/d\sin\alpha\sin\eta$$

$$G_{1012} = -\sqrt{2}\mu_c \sin\alpha/d$$

$$G_{1112} = -\sqrt{2}\mu_c [(1/D - \cos\eta/r)\cos\phi + (1/r - \cos\eta/D)\cos\beta + (\cos\beta\cos\eta - \cos\phi)/D]/\sin\eta$$

For the B_2 type:

$$G_{1313} = \mu_H + \mu_c (1 - \cos\alpha)$$

$$G_{1414} = \mu_H/d^2 + \mu_c [(1 - \cos\alpha)\{1 + D^2 (1/D - \cos\beta/d)^2\} - 2D\,(1/D - \cos\beta/d)(1 + \cos x)\}]/D^2\sin^2\beta$$

$$G_{1515} = \mu_H/d^2 + \mu_c (1/r - \cos\phi/d)^2 (1 - \cos\alpha)/\sin^2\phi + \mu_0\{(1 - \cos\alpha) + (1 + \cos x)\}/r^2\sin^2\phi$$

TABLE I

Force constants × 10^{-5} dynes/cm.					Frequencies					
	C_2H_4O	C_2D_4O	C_2H_4S	Type	C_2H_4O		C_2D_4O		C_2H_4S	
					Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
f_D	5·950	5·722	5·980		877	888	755	755	625	621
f_δ	5·130	4·880	4·900		1120	1125	970	970	1040	1037
f_r	4·590	4·530	4·250	A_1	1266	1288	1013	1013	1120	1113
f_α	0·610	0·610	0·580		1490	1533	1301	1297	1445	1448
f_η	0·984	0·921	0·625		3005	3054	2204	2249	2990	3018
f_θ	0·906	0·906	0·846		807	807	581	581	660	660
$f_\beta - f_{\beta\beta}$	0·557	0·557	0·517	A_2	(1345)	1294	1083	1090	..	(938)
$f_\phi - f_{\phi\phi}$	0·344	0·344	0·100		3063	3086	2250	2289	3080	3080
f_{dd}	0·330	0·080	0·100		892	892	809	809	711	711
f_{rr}	0·450	0·520	0·250	B_1	1153	1153	952	952	949	949
f_{dr}	0·145	0·145	0·140		1470	1442	1145	1145	1390	1380
$f_{d\alpha}$	0·079	0·079	0·075		3019	3047	2174	2141	2990	3011
$f_{d\beta}$	−0·185	−0·185	−0·180		821	821	577	577	686	686
$f_{d\phi}$	−0·185	−0·185	−0·090	B_2	1143	1149	896	919	823	826
					3079	3070	2317	2281	3080	3069

$$G_{1314} = -\mu_c (1/D - \cos\beta/d)(1 - \cos\alpha)/\sin\beta - (1 + \cos x)/D \sin\beta$$

$$G_{1315} = -\mu_c (1/r - \cos\phi/d)(1 - \cos\alpha)/\sin\phi$$

$$G_{1415} = \mu_H (\cos\eta - \cos\beta\cos\phi)/d^2 \sin\phi \sin\beta + \mu_c (1/r - \cos\phi/d)[(1/D - \cos\beta/d)(1 - \cos\alpha) - (1 + \cos x)/D]/\sin\phi \sin\beta.$$

5. Results

Using the elements of the F and G matrices given for the four species of vibrations, the secular equations are obtained for the three molecules in the usual way. These secular equations are then solved for the force constants, by the method of successive approximation. Frequencies are also calculated making use of the set of force constants which forms the best fit. The force constants obtained and the observed and calculated frequencies are presented in Table I.

It is easily seen that the agreement between the observed and calculated frequencies is fairly satisfactory. It may also be noted that the major force constants evaluated for the three molecules are very nearly the same, excepting that in the case of ethylene sulphide, slight changes are observed in the appropriate force constants when the oxygen is replaced by sulphur.

In the case of A_2 type vibrations in C_2H_4O the location of the frequency at 1345 cm.$^{-1}$ has been discussed by Lord and Nolin. This frequency is inactive in infra-red and its position in Raman effect is also not definite. In the present investigation, making use of the force constants given for the B_2 vibrations, this frequency has been found to be 1294 cm.$^{-1}$ In the case of ethylene sulphide this frequency works out to be 938 cm.$^{-1}$

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THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF FOUR SPIN SYSTEMS

I. The H^1 and F^{19} Resonance Spectra of 1-Fluoro, 2, 4-Dinitrobenzene†

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Abstract

High resolution H^1 and F^{19} nuclear magnetic resonance spectra of 1-fluoro, 2, 4-dinitrobenzene were obtained and analyzed to determine all the parameters involved. As the spectrum of one of the protons is well separated from that of the other two, the secular equation has been solved in the first approximation. The analysis gives the following spin-spin coupling constants: $J_0^{HH} = 8 \cdot 7 \pm 0 \cdot 3$ cps., $J_m^{HH} = 2 \cdot 9 \pm 0 \cdot 2$ cps., $J_p^{HH} = 0 \cdot 6 \pm 0 \cdot 3$ cps., $J_0^{HF} = 10 \cdot 4 \pm 0 \cdot 2$ cps., and the two meta H–F coupling constants were found to be considerably different being $6 \cdot 5 \pm 0 \cdot 3$ cps. and $3 \cdot 8 \pm 0 \cdot 3$ cps. It has been found that the *ortho* and *meta* H–F coupling constants have the same sign as the *ortho* and *para* H–H coupling constants.

Introduction

Analysis of nuclear magnetic resonance (NMR) spectra and the determination of the chemical shifts and the nuclear spin-spin coupling constants provide valuable information about the molecular electronic structure. Considerable amount of work[1–7] has been done recently on the spin-spin coupling constants of substituted benzenes and fluorobenzenes, and attempts[8] are also being made to understand these coupling constants on the basis of the electronic structure. In the present work the high resolution H^1 and F^{19} NMR spectra of 1-fluoro, 2, 4-dinitrobenzene were obtained and analyzed to determine all the parameters involved. The relative signs of the coupling constants were also determined.

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* Senior Research Fellow of the Council of Scientific and Industrial Research.

† This Paper is based on part of a thesis submitted by B. D. Nageswara Rao for a Ph.D. degree of Muslim University, Aligarh.

EXPERIMENTAL

The sample of 1-fluoro, 2, 4-dinitrobenzene, obtained from British Drug House, was used without further purification. The sample is contained in a sealed glass tube of about 5 mm. o.d. and about 15 cm. long. The H^1 and F^{19} spectra were obtained on a Varian V-4300 B High Resolution NMR Spectrometer with "Sample spinner" and "Superstabilizer"[9] at a fixed frequency of 40 Mc./sec. The general features of the instrument were described in an earlier publication.[10] Corresponding applied magnetic field intensities for H^1 and F^{19} resonance experiments are about 9,395 and 10,000 gauss respectively.

The line separations in the spectra were measured in cycles per second by the audiofrequency side-band technique.

By placing a capillary containing water inside the main sample tube, as an external standard, the chemical shifts of the proton resonance signals of the compound with reference to the signal from water were determined in the usual manner.

The H^1 and F^{19} resonance spectra are shown in Figs. 1 (*a*) and 2 (*a*) respectively.

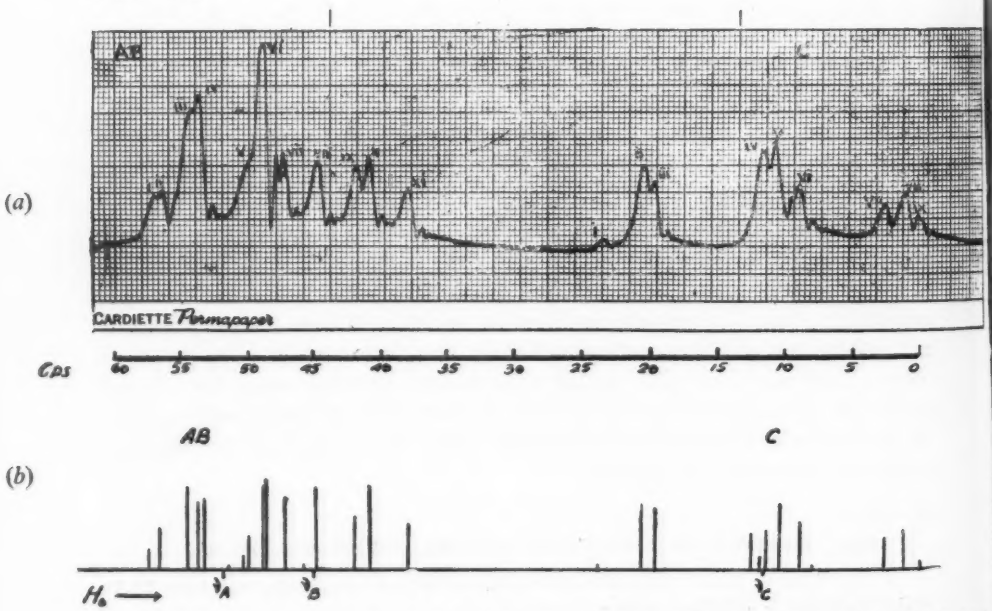


FIG. 1. H^1 NMR. Spectrum of 1-Fluoro, 2, 4-Dinitrobenzene at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated. 1 cm. = 4·051 cps.

THEORETICAL

The molecule 1-fluoro, 2, 4-dinitrobenzene is an unsymmetrical four-spin system, and is of the type ABCX[7], where all the nuclei are nonequivalent and all the coupling constants are different from one another. The theoretical spectrum is obtained on the basis of the general method given by McConnell, McLean and Reilly.[11] Taking the direction of the applied magnetic field to be the negative Z direction, the Hamiltonian of the system may be written as:

$$H = \sum_k \nu_k I_{zk} + \sum_{i<j} J_{ij} \vec{I}_i . \vec{I}_j \qquad (1)$$

in the usual notation.* Here all the energies are expressed in cycles per second to facilitate comparison with the observed frequencies, as the line separations are also measured in cycles per second.

All the zero order eigenfunctions and the corresponding diagonal matrix elements[12] for the ABCX type of molecule are given in Table I.

The non-vanishing off-diagonal matrix elements are:

$$\left.\begin{aligned} H_{23} &= H_{32} = H_{67} = H_{76} = H_{9,10} = H_{10,9} = H_{12,13} \\ &= H_{13,12} = \tfrac{1}{2} J_{BC} \\ H_{24} &= H_{42} = H_{68} = H_{86} = H_{9,11} = H_{11,9} = H_{12,14} \\ &= H_{14,12} = \tfrac{1}{2} J_{AC} \\ H_{34} &= H_{43} = H_{78} = H_{87} = H_{10,11} = H_{11,10} = H_{13,14} \\ &= H_{14,13} = \tfrac{1}{2} J_{AB} \end{aligned}\right\} . \qquad (2)$$

As the states with different values of I_{zx} do not mix, the basic product functions 5 and 15 (Table I) will become approximate stationary-state wave functions, and the corresponding diagonal matrix elements give the respective eigenvalues. Further, the states 6, 7 and 8 do not mix with the states 9, 10 and 11. But for a complete solution of the secular equation it is still necessary to solve four 3×3 determinants (for the states 2, 3 and 4; 6, 7 and 8; 9, 10 and 11; and 12, 13 and 14). Explicit expressions for the energy levels in these cases are difficult to derive and a systematic analysis is therefore not usually possible.

But the proton resonance spectrum of the molecule (Fig. 1 *a*) shows two groups of lines separated by about 40 cps. An approximate measure-

* The notation is the same as that used in reference 7.

TABLE I

Sl. No.	F_z	Basic function	Diagonal matrix element H_{nn}
1	2	$\alpha\alpha\alpha\alpha$	$\frac{1}{2}(\nu_A+\nu_B+\nu_C+\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}+J_{AX}+J_{BX}+J_{CX})$
2	1	$\alpha\alpha\beta\alpha$	$\frac{1}{2}(\nu_A+\nu_B-\nu_C+\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}+J_{AX}+J_{BX}-J_{CX})$
3	1	$\alpha\beta\alpha\alpha$	$\frac{1}{2}(\nu_A-\nu_B+\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}+J_{AX}-J_{BX}+J_{CX})$
4	1	$\beta\alpha\alpha\alpha$	$\frac{1}{2}(-\nu_A+\nu_B+\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}-J_{AX}+J_{BX}+J_{CX})$
5	1	$\alpha\alpha\alpha\beta$	$\frac{1}{2}(\nu_A+\nu_B+\nu_C-\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}-J_{AX}-J_{BX}-J_{CX})$
6	0	$\beta\beta\alpha\alpha$	$\frac{1}{2}(-\nu_A-\nu_B+\nu_C+\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}-J_{AX}-J_{BX}+J_{CX})$
7	0	$\beta\alpha\beta\alpha$	$\frac{1}{2}(-\nu_A+\nu_B-\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}-J_{AX}+J_{BX}-J_{CX})$
8	0	$\alpha\beta\beta\alpha$	$\frac{1}{2}(\nu_A-\nu_B-\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}+J_{AX}-J_{BX}-J_{CX})$
9	0	$\alpha\alpha\beta\beta$	$\frac{1}{2}(\nu_A+\nu_B-\nu_C-\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}-J_{AX}-J_{BX}+J_{CX})$
10	0	$\alpha\beta\alpha\beta$	$\frac{1}{2}(\nu_A-\nu_B+\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}-J_{AX}+J_{BX}-J_{CX})$
11	0	$\beta\alpha\alpha\beta$	$\frac{1}{2}(-\nu_A+\nu_B+\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}+J_{AX}-J_{BX}-J_{CX})$
12	−1	$\beta\beta\alpha\beta$	$\frac{1}{2}(-\nu_A-\nu_B+\nu_C-\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}+J_{AX}+J_{BX}-J_{CX})$
13	−1	$\beta\alpha\beta\beta$	$\frac{1}{2}(-\nu_A+\nu_B-\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}+J_{AX}-J_{BX}+J_{CX})$
14	−1	$\alpha\beta\beta\beta$	$\frac{1}{2}(\nu_A-\nu_B-\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}-J_{AX}+J_{BX}+J_{CX})$
15	−1	$\beta\beta\beta\alpha$	$\frac{1}{2}(-\nu_A-\nu_B-\nu_C+\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}-J_{AX}-J_{BX}-J_{CX})$
16	−2	$\beta\beta\beta\beta$	$\frac{1}{2}(-\nu_A-\nu_B-\nu_C-\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}+J_{AX}+J_{BX}+J_{CX})$

ment of the areas under the lines showed that one of the three protons gives rise to the well separated group of lines on the higher field side. If this proton is called C, this may also be treated similar to X as a first approximation. Then the basic product functions 2, 6, 9 and 12 (Table I) may also be considered as approximate stationary-state wave functions, and the diagonal matrix elements give the corresponding eigenvalues. Now only four 2×2 determinants remain to be solved, to obtain all the energy levels. The calculations can then be done by a straightforward extension of the method adapted for the ABX spectrum.[2, 3]

For convenience of calculation we define positive quantities D_+, F_+, F_- and D_- and angles θ_+, ϕ_+, ϕ_- and θ_- satisfying the following relations:

$$\left.\begin{aligned}
D_+ &= \tfrac{1}{2}\left[\{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AC} - J_{BC}) + (J_{AX} - J_{BX})\right]\}^2 + J_{AB}{}^2\right]^{\frac{1}{2}} \\
F_+ &= \tfrac{1}{2}\left[\{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AX} - J_{BX}) - (J_{AC} - J_{BC})\right]\}^2 + J_{AB}{}^2\right]^{\frac{1}{2}} \\
F_- &= \tfrac{1}{2}\left[\{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AC} - J_{BC}) - (J_{AX} - J_{BX})\right]\}^2 + J_{AB}{}^2\right]^{\frac{1}{2}} \\
D_- &= \tfrac{1}{2}\left[\{(\nu_A - \nu_B) + \tfrac{1}{2}\left[-(J_{AC} - J_{BC}) - (J_{AX} - J_{BX})\right]\}^2 + J_{AB}{}^2\right]^{\frac{1}{2}}
\end{aligned}\right\} \quad (3)$$

and

$$\left.\begin{aligned}
\tan 2\theta_+ &= \frac{J_{AB}}{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AC} - J_{BC}) + (J_{AX} - J_{BX})\right]} \\
\tan 2\phi_+ &= \frac{J_{AB}}{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AX} - J_{BX}) - (J_{AC} - J_{BC})\right]} \\
\tan 2\phi_- &= \frac{J_{AB}}{(\nu_A - \nu_B) + \tfrac{1}{2}\left[(J_{AC} - J_{BC}) - (J_{AX} - J_{BX})\right]} \\
\tan 2\theta_- &= \frac{J_{AB}}{(\nu_A - \nu_B) + \tfrac{1}{2}\left[-(J_{AC} - J_{BC}) - (J_{AX} - J_{BX})\right]}
\end{aligned}\right\}. \quad (4)$$

In terms of these quantities the mixed wave functions and the corresponding energy levels are obtained in explicit analytical form. The mixed states are labelled 3′, 4′, etc., to denote that these wave functions reduce to the basic product functions 3, 4, etc., when the chemical shift $(\nu_A - \nu_B)$ is large.

The different transitions are classified into AB, C and X types, and the transition frequencies with their relative intensities are given in Tables II (*a*), II (*b*) and II (*c*) respectively for the three types.* In the case of C and X transitions, only those combination lines with nonzero intensities are given.

* Similar expressions for the transition energies and relative intensities were obtained by Lee and Sutcliffe [*Trans. Farad. Soc.*, **54**, 308 (1958)] for the analysis of the spectra of 1: 1: 2-trifluoro, 1-bromo, 2-chloro ethane. The molecule was described as an **ABPX** system by these authors.

INTERPRETATION

(i) X *spectrum*

This corresponds to the F^{19} spectrum of the molecule. The theoretical spectrum given in Table II (*c*) shows that there are four strong lines symmetrically disposed about ν_X, and two doublets (transitions 3 and 4; and 6 and 7) with their centres separated by J_{CX}. The combination lines also form two such doublets, but as they are generally weak they may escape detection.

The expected strong lines are identified with (i), (v) and (viii) in the observed spectrum (Fig. 2 *a*), with the line (v) being assumed as a superposition of two strong lines. The two doublets are identified with lines (iii) and

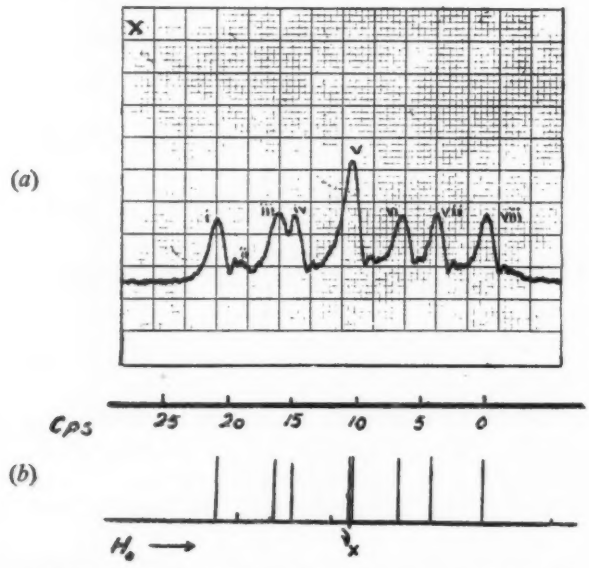


FIG. 2. F^{19} NMR Spectrum of 1-Fluoro 2, 4-Dinitrobenzene at 40 Mc/sec. (*a*) Experimental. (*b*) Calculated. 1 cm. = 4·821 cps.

(iv), and (vi) and (vii). But an unambiguous assignment of the lines to the transitions cannot be done unless the signs of coupling constants J_{CX} and $(J_{AX} + J_{BX})$ are known. By assuming the different possible combinations of signs for these constants, the following values were obtained:

$$| J_{CX} | = | J_{AX} + J_{BX} | = 10{\cdot}4 \pm 0{\cdot}2 \text{ cps.} \tag{5}$$

TABLE II (*a*)

AB *Transitions*

Sl. No.	Transition	Energy relative to $\frac{1}{2}(\nu_A + \nu_B)$	Relative intensity
1	$3' \rightarrow 1$	$\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) - D_+$	$1 + \sin 2\theta_+$
2	$4' \rightarrow 1$	$\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) + D_+$	$1 - \sin 2\theta_+$
3	$6 \rightarrow 3'$	$-\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) + D_+$	$1 + \sin 2\theta_+$
4	$6 \rightarrow 4'$	$-\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) - D_+$	$1 - \sin 2\theta_+$
5	$7' \rightarrow 2$	$\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) - F_+$	$1 + \sin 2\phi_+$
6	$8' \rightarrow 2$	$\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) + F_+$	$1 - \sin 2\phi_+$
7	$15 \rightarrow 7'$	$-\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) + F_+$	$1 + \sin 2\phi_+$
8	$15 \rightarrow 8'$	$-\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) - F_+$	$1 - \sin 2\phi_+$
9	$10' \rightarrow 5$	$\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) - F_-$	$1 + \sin 2\phi_-$
10	$11' \rightarrow 5$	$\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) + F_-$	$1 - \sin 2\phi_-$
11	$12 \rightarrow 10'$	$-\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) + F_-$	$1 + \sin 2\phi_-$
12	$12 \rightarrow 11'$	$-\frac{1}{2}J_{AB} + \frac{1}{4}(J_{BC} + J_{AC} - J_{AX} - J_{BX}) - F_-$	$1 - \sin 2\phi_-$
13	$13' \rightarrow 9$	$\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) - D_-$	$1 + \sin 2\theta_-$
14	$14' \rightarrow 9$	$\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) + D_-$	$1 - \sin 2\theta_-$
15	$16 \rightarrow 13'$	$-\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) + D_-$	$1 + \sin 2\theta_-$
16	$16 \rightarrow 14'$	$-\frac{1}{2}J_{AB} - \frac{1}{4}(J_{BC} + J_{AC} + J_{AX} + J_{BX}) - D_-$	$1 - \sin 2\theta_-$

And

$$\left.\begin{aligned} 2\,|\,D_+ - F_-\,| &= 1{\cdot}2 \pm 0{\cdot}2 \text{ cps. or } 2{\cdot}6 \pm 0{\cdot}2 \text{ cps.} \\ 2\,|\,D_- - F_+\,| &= 2{\cdot}6 \pm 0{\cdot}2 \text{ cps. or } 1{\cdot}2 \pm 0{\cdot}2 \text{ cps.} \end{aligned}\right\} \qquad (6)$$

according as J_{CX} is positive or negative respectively.

The weak line (ii) is one of the four combination lines and its final assignment is made later.

TABLE II (*b*)

C *Transitions*

Sl. No.	Transition	Energy	Relative intensity
1	2→ 1	$\nu_c + \frac{1}{2}(J_{BC} + J_{AC} + J_{CX})$	1
2	7′→ 3′	$\nu_c + \frac{1}{2}J_{CX} + (D_+ - F_+)$	$\cos^2(\phi_+ - \theta_+)$
3	8′→ 4′	$\nu_c + \frac{1}{2}J_{CX} - (D_+ - F_+)$	$\cos^2(\phi_+ - \theta_+)$
4	8′→ 3′	$\nu_c + \frac{1}{2}J_{CX} + (D_+ + F_+)$	$\sin^2(\phi_+ - \theta_+)$
5	7′→ 4′	$\nu_c + \frac{1}{2}J_{CX} - (D_+ + F_+)$	$\sin^2(\phi_+ - \theta_+)$
6	9→ 5	$\nu_c + \frac{1}{2}(J_{BC} + J_{AC} - J_{CX})$	1
7	15→ 6	$\nu_c - \frac{1}{2}(J_{BC} + J_{AC} - J_{CX})$	1
8	13′→10′	$\nu_c - \frac{1}{2}J_{CX} + (F_- - D_-)$	$\cos^2(\phi_- - \theta_-)$
9	14′→11′	$\nu_c - \frac{1}{2}J_{CX} - (F_- - D_-)$	$\cos^2(\phi_- - \theta_-)$
10	14′→10′	$\nu_c - \frac{1}{2}J_{CX} + (F_- + D_-)$	$\sin^2(\phi_- - \theta_-)$
11	13′→11′	$\nu_c - \frac{1}{2}J_{CX} - (F_- + D_-)$	$\sin^2(\phi_- - \theta_-)$
12	16→12	$\nu_c - \frac{1}{2}(J_{BC} + J_{AC} + J_{CX})$	1

(Transitions 2, 3, 8 and 9 represent combination lines.)

By comparing the value of J_{CX} obtained here with the H–F coupling constants observed by earlier workers,[2,6] the proton which is *ortho* to fluorine is identified with C. Then J_{AX} and J_{BX} are the *meta* H–F coupling constants.

(ii) C *spectrum*

The theoretical spectrum of C, given in Table II (*b*), can be subdivided for convenience of identification, in a manner exactly similar to the case of the X spectrum. But the combination lines in this case may be considerably stronger than in the case of X, as the chemical shift of C with respect to AB is not very large.

The expected strong lines are identified with the lines (ii), (iv), (v) and (viii) of the observed spectrum (Fig. 1 *a*), but again the proper assignment depends on the signs of the coupling constants J_{CX} and $(J_{BC} + J_{AC})$ so that

TABLE II (*c*)

X *Transitions*

Sl. No.	Transition	Energy	Relative intensity
1	5→ 1	$\nu_x + \frac{1}{2}(J_{AX} + J_{BX} + J_{CX})$	1
2	9→ 2	$\nu_x + \frac{1}{2}(J_{AX} + J_{BX} - J_{CX})$	1
3	10′→ 3′	$\nu_x + \frac{1}{2}J_{CX} + (D_+ - F_-)$	$\cos^2(\phi_- - \theta_+)$
4	11′→ 4′	$\nu_x + \frac{1}{2}J_{CX} - (D_+ - F_-)$	$\cos^2(\phi_- - \theta_+)$
5	12→ 6	$\nu_x - \frac{1}{2}(J_{AX} + J_{BX} - J_{CX})$	1
6	13′→ 7′	$\nu_x - \frac{1}{2}J_{CX} + (F_+ - D_-)$	$\cos^2(\phi_+ - \theta_-)$
7	14′→ 8′	$\nu_x - \frac{1}{2}J_{CX} - (F_+ - D_-)$	$\cos^2(\phi_+ - \theta_-)$
8	16→ 15	$\nu_x - \frac{1}{2}(J_{AX} + J_{BX} + J_{CX})$	1
Combination lines			
9	11′→ 3′	$\nu_x + \frac{1}{2}J_{CX} + (D_+ + F_-)$	$\sin^2(\phi_- - \theta_+)$
10	10′→ 4′	$\nu_x + \frac{1}{2}J_{CX} - (D_+ + F_-)$	$\sin^2(\phi_- - \theta_+)$
11	14′→ 7′	$\nu_x - \frac{1}{2}J_{CX} + (F_+ + D_-)$	$\sin^2(\phi_+ - \theta_-)$
12	13′→ 8′	$\nu_x - \frac{1}{2}J_{CX} - (F_+ + D_-)$	$\sin^2(\phi_+ - \theta_-)$

as in the case of the X spectrum, only the magnitudes of these are determined. They are

$$|J_{CX}| = 10{\cdot}2 \pm 0{\cdot}2 \text{ cps.}; \quad |J_{BC} + J_{AC}| = 9{\cdot}3 \pm 0{\cdot}2 \text{ cps.} \qquad (7)$$

The value of J_{CX} obtained here agrees well with that in Eq. 5 thus providing a check on the assignment.

The doublets in the C spectrum are checked after the AB spectrum has been analyzed.

(iii) AB *spectrum*

The theoretical AB spectrum given in Table II (*a*) consists of four quartets, which may be called D_+ quartet, F_+ quartet, F_- quartet and D_- quartet respectively. The frequency and intensity distributions in every

one of these quartets are just similar to the quartets in ABX type of spectra.[2, 3] The frequencies of the quartet centres, with reference to $\frac{1}{2}(\nu_A+\nu_B)$, are given by

$$\left.\begin{aligned} &\tfrac{1}{4}[(J_{BC}+J_{AC})+(J_{AX}+J_{BX})]\\ &\tfrac{1}{4}[(J_{AX}+J_{BX})-(J_{BC}+J_{AC})]\\ &\tfrac{1}{4}[(J_{BC}+J_{AC})-(J_{AX}+J_{BX})]\\ &\tfrac{1}{4}[-(J_{BC}+J_{AC})-(J_{AX}+J_{BX})] \end{aligned}\right\}. \tag{8}$$

Each one of the quartets consists of a pair of doublets whose separation is J_{AB}, and the separation between alternate lines in a quartet is $2D_+$, or $2F_+$, etc., according as it is a D_+ quartet or F_+ quartet, etc.

As the frequencies of AB spectrum remain unchanged if J_{AB} is replaced by $-J_{AB}$, only $|J_{AB}|$ can be found from the analysis.

From the observed frequencies, by trial and error, three quartets were first picked up with centres at 44·2, 49·3 and 53·7 cps. The separations between alternate lines in these quartets are 9·1, 11·6 and 4·3 cps. respectively. From these three quartets it was found that

$$|J_{AB}| = 2{\cdot}9 \pm 0{\cdot}2 \text{ cps.} \tag{9}$$

For the fourth quartet it was necessary to assume that the two central lines coincide, within experimental error, to form a single strong line and this was identified with line (vi) in the spectrum. Now from the intensity expressions it will be seen that in this case the two outer lines of the quartet would have zero intensity, *i.e.*, the quartet reduces to a single intense line. This was supported by the fact that no lines were observed separated by 2·9 cps. on either side from the line (vi).

(iv) *Signs of the coupling constants*

The four quartets in the AB spectrum may be assigned as D_+ quartet, F_+ quartet, etc., depending on the frequencies of their centres. But this in turn depends on the signs of $(J_{BC}+J_{AC})$ and $(J_{AX}+J_{BX})$ which are not known. If ν_a, ν_b, ν_c and ν_d are the frequencies of the four quartet centres, such that $\nu_a < \nu_b < \nu_c < \nu_d$, by assuming different combinations of signs of $(J_{BC}+J_{AC})$ and $(J_{AX}+J_{BX})$, the following assignments are possible:

TABLE III

Sl. No.	Sign of $J_{BC} + J_{AC}$	Sign of $J_{AX} + J_{BX}$	Assignment of quartet ν_α	ν_β	ν_γ	ν_δ	Inferred sign of J_{CX}
1	+	+	D_-	F_-	F_+	D_+	+
2	+	−	F_+	D_+	D_-	F_-	+
3	−	+	F_-	D_-	D_+	F_+	−
4	−	−	D_+	F_+	F_-	D_-	−

By comparing the values of $|D_+ - F_-|$ and $|D_- - F_+|$ for all the four assignments with those obtained in the analysis of X spectrum the corresponding sign of J_{CX} is inferred in each case. This is given in the last column of Table III.

The correct assignment among these four may be found by calculating the frequencies of the doublets in C spectrum and the weak combination line in X spectrum and comparing with the observed frequencies. On doing so, it was found that only the assignments 1 and 4 would give satisfactory agreement, thus ruling out assignments 2 and 3 in Table III. It is thus concluded that $(J_{BC} + J_{AC})$, $(J_{AX} + J_{BX})$ and J_{CX} are all of the same sign.

These two assignments (1 and 4 in Table III) give the same frequencies and intensities for AB, C and X spectra.

The calculated H^1 and F^{19} resonance spectra for the molecule are shown in Figs. 1 (*b*) and 2 (*b*) respectively. The line heights are drawn roughly proportional to the calculated relative intensities. The parameters in Eq. (11) are used for calculation. It may be noted that in the observed spectrum the intensities are given by the areas under the lines. Considering the approximation made in the calculation of the energy levels, the agreement between observed and calculated spectra is quite satisfactory.

RESULTS

The values of $(\nu_A - \nu_B)$, $(J_{BC} - J_{AC})$ and $(J_{AX} - J_{BX})$ are obtained for assignment 1* (Table III) by first calculating $D_+ \cos 2\theta_+$, $F_+ \cos 2\phi_+$, $F_- \cos 2\phi_-$† and $D_- \cos 2\theta_-$. They are found to be

* Calculation on the basis of assignment 4 only reverses the sign of the coupling constants J_{BC}, J_{AC}, J_{AX} and J_{BX}.

† $F_- \cos 2\phi_-$ becomes zero, as $J_{AB} = 2F_-$, according to this assignment. But this was not used in the calculation as $F_- \cos 2\phi_-$ is highly sensitive to small errors in F_-.

$$\left.\begin{aligned}(\nu_A - \nu_B) &= 5{\cdot}9 \pm 0{\cdot}3 \text{ cps.}\\ (J_{BC} - J_{AC}) &= 8{\cdot}0 \pm 0{\cdot}3 \text{ cps.}\\ (J_{AX} - J_{BX}) &= 2{\cdot}7 \pm 0{\cdot}3 \text{ cps.}\end{aligned}\right\}. \qquad (10)$$

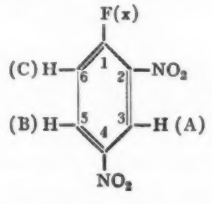
The factors $D_+ \cos 2\theta_+$ etc., can also be negative, but this only interchanges the roles of A and B in the above values.

All the different parameters can be summarized as

$$\left.\begin{aligned}\nu_A - \nu_{H_2O} &= 136{\cdot}9 \pm 0{\cdot}5\ddagger \text{ cps.}\\ \nu_A - \nu_C &= 41{\cdot}2 \pm 0{\cdot}3 \text{ cps.}\\ \nu_B - \nu_C &= 35{\cdot}3 \pm 0{\cdot}3 \text{ cps.}\\ |J_{AB}| &= J_m^{HH} = 2{\cdot}9 \pm 0{\cdot}2 \text{ cps.}\\ J_{BC} &= J_0^{HH} = 8{\cdot}7 \pm 0{\cdot}3 \text{ cps.}\\ J_{AC} &= J_P^{HH} = 0{\cdot}6 \pm 0{\cdot}3 \text{ cps.}\\ J_{AX} &= J_m^{HF} = 6{\cdot}5 \pm 0{\cdot}3 \text{ cps.}\\ J_{BX} &= J_m^{HF} = 3{\cdot}8 \pm 0{\cdot}3 \text{ cps.}\\ \text{and } J_{CX} &= J_0^{HF} = 10{\cdot}4 \pm 0{\cdot}2 \text{ cps.}\end{aligned}\right\}. \qquad (11)$$

The *ortho* and *meta* H–F coupling constants have the same sign as the *ortho* and *para* H–H coupling constants. This supports the observation of Bak, Shoolery and Williams[6] in the case of deuterated fluorobenzenes. The values of coupling constants obtained here also favourably compare with those obtained by earlier workers. But the two *meta* H–F coupling constants (J_{AX} and J_{BX}) obtained here differ considerably from one another.

As J_{AC} represents the *para* H–H coupling constant when $(\nu_A - \nu_B)$ is positive, we find that the proton *para* to C (*i.e.*, at the position 3) is least-shielded of the three protons in the molecule. Thus the three protons are identified from the analysis. That the A, B, and C protons as given in Fig. 3, are shielded in the increasing order of magnitude, is in conformity with the results obtained on the chemical shifts of *ortho*, *meta* and *para* protons in substituted benzenes by Corio and Dailey.[13]



‡ The bulk diamagnetic susceptibility correction is not applied.

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LATITUDE DEPENDENCE OF THE DAILY VARIATION OF COSMIC RAY INTENSITY

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Abstract

The yearly average daily variation curves for the period July 1957 to June 1958 for data from neutron monitors operated at various places during the I.G.Y. are harmonically analysed. Data for different latitude belts are grouped together. The amplitude and hour of maximum of the first harmonic show a marked latitude dependence. It is found, however, that stations in the same latitude belt show large differences in amplitudes. Possible reasons for such differences are discussed. It is concluded that these differences are due to extraneous unspecified factors and the published data are not suitable for analysis without further scrutiny.

I. Introduction

The study of the latitude dependence of the amplitude and phase of daily variation of cosmic ray intensity provides an important tool for studying the energy spectrum of the primary anisotropy responsible for the daily variation. Using data obtained from ionisation chambers for cosmic ray meson intensity, Dorman[1] has calculated the energy spectrum for the period 1937–51.

During the recent I.G.Y., cosmic ray meson telescopes and neutron monitors have been operated at several places in the world by various research groups. This has provided a unique opportunity for conducting studies like the latitude dependence of the nature of the daily variation of cosmic ray intensity.

With this objective in view, we examined recently the available I.G.Y. data. As the meteorological corrections for the meson intensity are complicated and the temperature correction involved therein is uncertain, we concentrated our attention only on data obtained from neutron monitors. However, in view of the discrepancies observed and reported by one of us

(R. P. Kane)[2] for the I.G.Y. neutron data, the emphasis in the present analysis has been more on checking the validity of basic data for a study of this type than on drawing conclusions about the latitude dependence of the daily variation.

II. Details of Stations Supplying Neutron Monitor Data

The data utilised are taken from the recent publication[3] *Cosmic Ray Intensity during the I.G.Y. Nos.* 1 *and* 2 published by the Japanese workers and are in the logarithmic representation form which was first introduced by Wada.[4] Details of 34 stations for which data were available for all the 12 months (July 1957 to June 1958) are given in Table I.

III. Latitude Dependence of the Daily Variation

For studying the daily variation, the yearly average curves for neutron monitor at various stations were harmonically analysed. It was found that except for some equatorial stations for which the amplitudes of the 1st and 2nd harmonics were comparable, the first harmonic was the most predominent one. The 3rd and higher harmonics were negligibly small in all cases. The amplitudes and hours of maxima (L.T.) of the first and second harmonic are given in Table I.

For a study of the latitude dependence of the daily variation, we have chosen the predominent harmonic, *viz.*, the first harmonic, of the daily variation. Since the form of the daily variation is known to be changing radically from day-to-day it is desirable that comparison of data from different stations should be only for common days. It was found, however, that the number of days common for *all* the stations was less than 30 during the twelve months under consideration and was too small to give results statistically accurate enough to enable comparison of any two stations. Hence, the stations were grouped according to their geomagnetic latitudes in several latitude belts and it was ensured that in any belt, data for all stations were for common days. The latitude belts and the number of common days in each of them are indicated in column one of Table I.

Figure 1 is a plot of the amplitude and hour of maxima of the first harmonic of the daily variation for different geomagnetic latitudes. Each point represents the average for a latitude belt. High altitude stations are indicated by crosses. The broad conclusions that could be drawn from Fig. 1 and Table I are as follows:—

(1) The latitude dependence of the amplitude and phase of the daily variation is different for the northern and the southern hemisphere. The features may be compared latitude-wise as shown in Table II.

TABLE I

Amplitudes and hours of maxima of the first harmonic of the daily variation of neutron intensity recorded at various stations

Belt No. (Common days)	Station	Geomagnetic Lat.	Geomagnetic Long.	Alt. (Met.)	Cut off energy (BeV)	Mean energy (BeV)	Baro. pressure coeff. %/mb.	First harmonic Amplitude R_1%	First harmonic Hr. of maximum (L.T.)	Second harmonic Amplitude R_2%	Second harmonic Hr. of maximum (L.T.)	Ratio R_1/R_2
1 (265)	Thule ..	88°	1°	S.L.	0	11·5	0·74	0·115±0·012	12·0	0·044±0·012	9·3	3·0
	Resolute ..	83°	289°	S.L.	0	11·5	0·73	0·173±0·013	17·4	0·015±0·013	7·9	8·5
2 (291)	Murchison Bay ..	72°	137°	S.L.	0·1	11·5	0·74	0·158±0·011	13·4	0·017±0·011	8·2	8·0
	Churchill ..	70°	323°	39	0·3	11·5	0·73	0·293±0·013	14·4	0·023±0·013	4·7	14·5
3 (328)	Sulphur Mountain	58°	300°	2283	1·1	9·7	0·83	0·284±0·005	14·4	0·061±0·005	5·7	4·7
	Mt. Washington ..	56°	356°	1917	1·9	9·7	0·74	0·357±0·006	13·0	0·040±0·006	2·1	9·0
4 (228)	Uppsala ..	59°	106°	S.L.	1·3	12·1	0·74	0·301±0·012	13·6	0·053±0·012	5·1	6·0
	Deep River ..	58°	358°	145	1·3	12·1	0·71	0·338±0·009	14·1	0·061±0·009	1·7	5·7
	Ottava ..	57°	351°	101	1·7	12·1	0·72	0·266±0·015	14·7	0·026±0·015	6·3	9·0
	Leeds ..	56°	83°	100	1·6	12·1	0·68	0·305±0·015	15·3	0·070±0·015	4·4	4·4
	London ..	54°	84°	S.L.	2·1	12·1	0·72	0·192±0·011	12·6	0·043±0·011	8·1	4·8
	Herstmonceux ..	54°	84°	23	2·2	12·1	0·77	0·282±0·009	12·7	0·027±0·009	0·2	9·3
5 (276)	Gottingen ..	52°	94°	273	2·4	12·1	0·72	0·320±0·010	13·1	0·023±0·010	6·5	16·0
	Weissenau ..	49°	92°	427	3·2	12·1	0·78	0·440±0·011	12·9	0·042±0·011	5·2	7·5
	Chicago ..	53°	337°	S.L.	2·4	12·1	0·72	0·257±0·012	13·9	0·073±0·012	3·3	3·7
	Lincoln ..	51°	326°	350	2·6	12·1	0·72	0·281±0·013	14·4	0·035±0·013	8·1	7·0
	Yakutsk ..	51°	194°	105	2·2	12·1	0·72	0·242±0·014	14·4	0·075±0·014	1·6	3·0
6 (319)	Climax ..	48°	316°	3400	3·0	9·7	0·73	0·293±0·003	15·5	0·044±0·003	5·1	7·3
	Zugspitze ..	48°	92°	2960	3·3	9·7	0·79	0·422±0·003	13·6	0·018±0·003	0·0	21·0
7 (325)	Berkley ..	44°	298°	S.L.	4·2	12·5	0·72	0·364±0·010	14·6	0·158±0·010	1·8	2·9
	Rome ..	43°	92°	60	4·7	12·5	0·72	0·329±0·013	12·8	0·092±0·013	0·7	3·7

8 (311)	Alma Ata ..	33°	151°	806	7·3	25·1	0·72	0·254±0·009	13·1	0·015±0·009	7·6	12·5
9 (360)	Mt. Norikura ..	26°	204°	2770	10·3	25·0	0·64	0·303±0·005	13·5	0·067±0·005	6·7	4·3
10 (280)	Makapuu Point ..	21°	267°	S.L.	11·6	29·0	0·72	0·238±0·013	9·3	0·118±0·013	5·2	2·0
11 (227)	Ahmedabad ..	14°	144°	S.L,	13·7	31·0	0·72	0·360±0·024	12·3	0·140±0·024	8·4	2·6
12 (111)	Kodaikanal ..	1°	147°	2343	15·5	33·8	0·72	0·276±0·020	12·7	0·361±0·020	9·9	0·8
	Huancayo ..	− 1°	354°	3400	13·2	33·8	0·73	0·236±0·007	12·2	0·039±0·007	2·5	6·0
	Mina Aguilar ..	−12°	3°	4000	11·8	31·0	0·71	0·250±0·006	11·8	0·121±0·006	3·4	2·1
13 (322)	Lae ..	−16°	217°	S.L.	13·5	29·0	0·72	0·208±0·018	9·0	0·325±0·018	7·1	0·6
14 (283)	Buenos Aires ..	−23°	9°	S.L	9·4	27·0	0·71	0·171±0·012	11·4	0·077±0·012	11·7	2·1
15 (281)	Hermanus ..	−34°	82°	S.L.	7·0	25·0	0·72	0·119±0·013	3·3	0·109±0·013	7·8	1·1
16 (204)	Ushuaia ..	−43°	1°	S.L.	4·2	20·0	0·71	0·167±0·013	12·0	0·054±0·013	2·5	3·4
17 (340)	Mt. Wellington ..	−52°	225°	725	2·0	12·1	0·71	0·309±0·008	13·7	0·080±0·008	7·2	3·9
18 (347)	Mawson ..	−73°	104°	S.L.	0·2	11·5	0·71	0·234±0·009	16·9	0·004±0·009	0·6	59·0

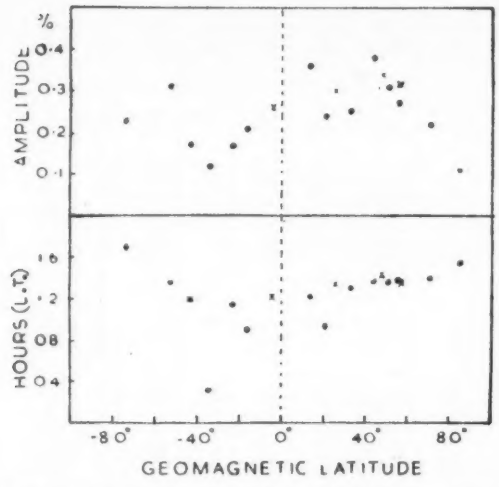

FIG. 1. Latitude dependence of the amplitude and hour of maximum of the first harmonic of the daily variation. High altitude stations are indicated by crosses.

TABLE II

Latitude region	Northern hemisphere		Southern hemisphere	
	Amp.	Hour of Max.	Amp.	Hour of Max.
Equator	0·25%	Noon	0·25%	Noon
10–40°	0·25%	Becomes 2 hours earlier	0·15%	Becomes several hours earlier
40–60°	Increases to 0·35%	Noon	Increases to 0·30%	Noon
60–90°	Drops below 0·15%	Noon	Indication of a drop	Becomes later than Noon by more than 4 hours

It seems, therefore, that a reduction in amplitude and shifting of the hour of maximum to earlier hours at about 20–40° latitude is a feature much more prominent in the southern hemisphere. Also, the hour of maximum advances with latitude after about 40° in the southern hemisphere but not appreciably in the northern hemisphere.

(2) There is no significant difference of amplitude or hour of maximum between high latitude and sea-level stations at the same latitude.

(3) For high latitude stations, the first harmonic is the only prominent one. For equatorial stations the second harmonic also gains prominence.

If the pattern of latitude dependence of the daily variation of cosmic ray intensity as discussed above is genuine, attempts could be made to invoke physical models of solar beams or modulation mechanisms to explain the various experimental facts and to estimate the energy spectrum of the primary antisotropy. There are, however, a few disconcerting features revealed by the above analysis. Firstly, there are not enough stations in the southern hemisphere to confirm the peculiar pattern exhibited by the existing stations. Secondly, stations in the same latitude belts in the northern hemisphere are not showing similar daily variation characteristics. In fact, differences in the amplitudes of stations in the same belt are sometimes more than the differences in amplitudes of stations in different belts. Under these circumstances, it would be meaningless to attempt a theoretical interpretation of the average results shown in Fig. 1. Instead, attention should be paid to the differences between stations in the same latitude belts which have, therefore, the same energy responses, and possible reasons for these differences should be examined. We have examined below some of the possible causes that could give rise to these differences.

IV. Causes of Differences between Comparable Stations

(*a*) *Statistical Errors*

It will be seen from Table I that the statistical errors associated with the amplitudes are very small and the extreme differences between amplitudes of stations in the same belt are statistically significant even on a 3σ level. Recently, McCracken[5] and Dyring[6] have shown that for various instrumental reasons, the standard error associated with data from neutron monitors is 1·2 times the usual Poisson standard error. It will be seen however that the differences referred to above far exceed 3σ level with even such an enhanced standard error. It seems, therefore, that statistical errors cannot account for the observed differences.

(*b*) *Method of Data Processing*

As shown in a previous communication,[2] utilisation of data presented in the logarithmic form does not produce discrepancies exceeding 0·01%.

(*c*) *Longitude Differences*

Since the anisotropy causing daily variation is of a transient nature, the daily variation recorded by stations differing in longitudes may not be similar on individual days. However, on an yearly average basis, such differences are likely to even out and stations at different longitudes but in the same latitude belt are expected to show similar average daily variations.

It will be seen from Table I that for many pairs of stations, the latitudes, longitudes and altitudes are almost alike. Even in these cases, the amplitudes are different. This indicates that the amplitude differences are not related to longitude differences.

(*d*) *Improper Pressure Corrections*

Discrepancies due to improper pressure corrections can be of various types.

(*i*) *Errors due to linear pressure correction.*—The absorption of nucleonic component is an exponential function of barometric pressure. If, therefore, a linear pressure correction is applied, considerable errors are introduced (Dorman *et al.*[7]) when pressure values have large deviations from mean. Since, however, the yearly average daily variation of pressure has amplitudes less than 2–3 mb., the errors due to linear pressure correction would be negligible.

(*ii*) *Differences in pressure coefficients.*—As can be seen from Table I, the barometric coefficients used range from 0·64–0·83% per mb. Hg. However, for stations in the same belt, the coefficients do not differ by more than 0·1% in any belt. Since, the first harmonic of yearly average daily variation of pressure is less than 0·5 mb. at most of the stations in high latitudes, a maximum discrepancy of ·05% is expected on this account.

(*iii*) *Errors in pressure recordings.*—For most of the stations, barometric pressure values are obtained from microbarographs. A common trouble with these instruments is the friction between the pen and the paper which results into confining the pen to the mean pressure level and indicating reduced pressure ranges. This can be checked by comparing the daily pressure range (difference between maximum and minimum pressure) as read on the microbarograph with the range observed with a standard barometer. If friction is suspected, it can be overcome by adjusting the pen to rest on the paper lightly or, failing this, by arranging for the pen to be mechanically lifted off the paper for a few seconds at regular intervals.

(*e*) *Faulty Basic Data*

Unless the amplitude differences are caused by improper meteorological corrections, one would suspect that these discrepancies occur due to faulty basic data. In an earlier communication[2] one of us (R. P. Kane) has shown that when the bi-hourly percentage values of two stations of about the same latitude, longitude and altitude are compared, they show in the cases of many pairs, differences of the order of a few per cent. which can be explained as only due to faults in the basic data. It seems from the present analysis that these differences do not even out even in the case of yearly average curves.

V. Conclusion

It is concluded from the present analysis that the data for neutron monitors operated during the I.G.Y. show discrepancies when their yearly average daily variation curves are compared. The published data are, in general, not suitable without further scrutiny for studies of the energy dependence of the daily variation of cosmic ray intensity.

The authors are grateful to Dr. V. A. Sarabhai for helpful discussions and valuable criticism. Thanks are due to the Atomic Energy Commission of India for financial assistance.

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LEVELS IN Co^{59}

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Introduction

The work regarding the β-decay of Fe^{59} [Metzger, (1952) and Ferguson (1959)] has established the existence of levels in Co^{59} at 1097 Kev, and 1289 Kev which are fed by strong β-groups. Ferguson (1959) inferred the existence of 140 Kev and 330 Kev transitions from a scintillation spectrometer study. Some additional and confirmatory information obtained with the intermediate image β-ray spectrometer and a scintillation spectrometer is presented here.

Experimental Procedure and Results

The $Fe_2^{59}O_3$ sample was supplied by Oak Ridge National Laboratory and proved to be pure Fe^{59} from the characteristic β- and γ-radiations following a half-life of $46{\cdot}5 \pm 1$ days.

β-ray sources were prepared by evaporation of a drop from a fine suspension of the sample in distilled water on an aluminium foil ($\sim 150\,\mu$ gm./cm.^{2}). β-spectra were observed using a thin counter window ($\sim 70\,\mu$ gm./cm.^{2} collodion) in the intermediate image β-ray spectrometer. They were corrected for counter window absorption and backscattering [Subba Rao (1960)]. Kurie plots of these β-spectra are shown in Fig. 1. The presence of a β-group of maximum energy 150 ± 10 Kev is clearly seen. Table I summarises the results of the analysis of β-spectra.

A careful search for internal conversion lines indicated only the presence of a weak line corresponding to internal conversion in all the shells of Co^{59} of a 70 kev transition. The intensity of this line relative to the total β-spectrum is $(0{\cdot}25 \pm 0{\cdot}07)\%$. This conversion line is shown in Fig. 2 (A).

Figures 2 (B) and 2 (C) show the low energy and high energy parts of the γ-spectrum of Fe^{59} respectively observed with a $1\frac{1}{2}'' \times 1\frac{1}{2}''$ NaI (Tl) crystal optically coupled to a Dumont 6292 photomultiplier. In the observation of the low energy part, Fig. 2 (B), only a 5 mm. thick perspex absorber was used

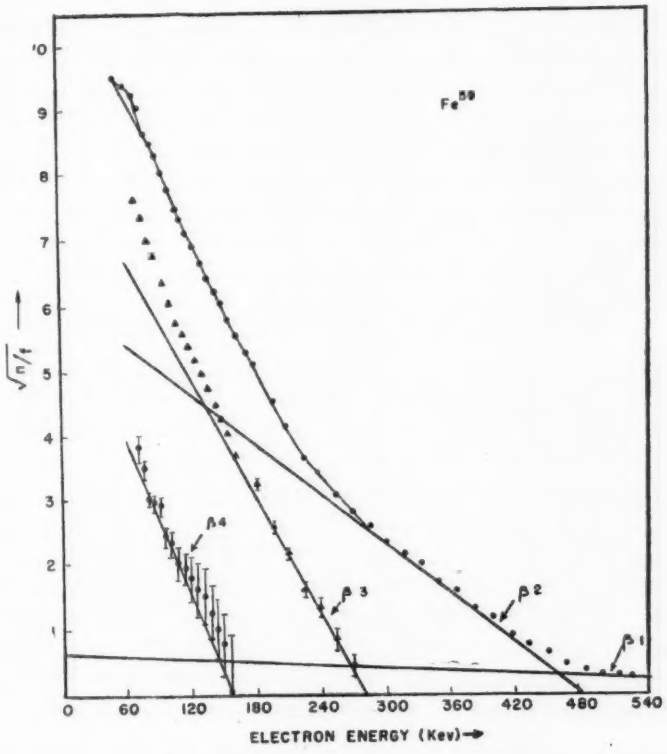

FIG. 1. Kurie plots of β-spectra of Fe^{59}

TABLE I

β-group	Maximum Energy (Kev)	Relative Intensity (%)	log ft.	Nature of β-transition
β_1	1580 ± 20	$1 \pm 0{\cdot}4$	9·2	Second forbidden
β_2	470 ± 6	52 ± 2	6·6	First forbidden or "Hindered" allowed
β_3	280 ± 6	42 ± 2	5·8	Allowed
β_4	150 ± 10	$5 \pm 1{\cdot}5$	5·6	Allowed

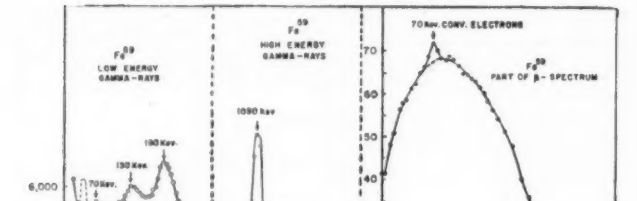

FIG. 2. (A) Internation conversion line corresponding to a 70 Kev transition.
(B) Low energy γ-rays.
(C) High energy γ-rays.

to cut off β-radiation. A 70 Kev γ-ray, which can be identified with the internal conversion line in Fig. 2 (A), is clearly seen. There is no possibility of a misinterpretation of any scattered peak due to higher energy γ-rays or X-rays from any absorbers. No possible impurities which have a 70 Kev γ-ray could be found in the neighbourhood of Fe with such half-life. From these considerations, it is proposed that a 70 Kev transition exists in addition to the 135 Kev, 190 Kev, 330 Kev, 1100 Kev and 1290 Kev transitions. The relative intensities of 70 and 135 Kev γ-rays are $\gamma_{70}/\gamma_{135} = 0{\cdot}5 \pm 0{\cdot}2$.

The relative intensity of the 1097 and 1290 Kev γ-rays has been determined by photoelectron spectrum (with gold converter) and by the scintillation spectrometer. The evaluation of the relative intensity is much facilitated by the availability of standard Co^{60} γ-rays in the same energy region. The average of the two methods gave $\gamma_{1100}/\gamma_{1290} = 1{\cdot}26 \pm 0{\cdot}06$ in good agreement with the results of Metzger (1952) and Ferguson (1959). The relative intensity of the 70 Kev γ-ray observed here, together with the intensity determinations of Ferguson (1959) yield $\gamma_{70}/(\gamma_{1100} + \gamma_{1290}) = (0{\cdot}42 \pm 0{\cdot}2)\%$. From the intensities of β-groups and the fact that the 1100 Kev and 1290 Kev γ-rays are very little converted, it is found that $(\gamma_{1100} + \gamma_{1290}$ is $(0{\cdot}96 \pm 0{\cdot}03)$ of the total β-disintegration rate. Combined with the observed relative conversion electron intensity of 70 Kev transition, $\alpha_{70}^{\text{total}} = 0{\cdot}6 \pm 0{\cdot}45$. Even such a rough estimate when compared with theoretical values [Rose, 1958] indicates that this transition does not involve a change of more than two units of angular momentum.

Discussion

The spin of the ground state of Co^{59} has been measured to be 7/2. From the γ-γ angular correlation of 199 and 1097 Kev, and with the aid of conversion coefficients, the spins of the 1097 Kev and 1289 Kev excited states were inferred to be 5/2— and 3/2—, [Metzger (1952)]. These assignments have been indentified with the *j-j* coupling shell model states $f_{7/2}$, $f_{5/2}$ and $p_{3/2}$ respectively. From the recent finding of 143 Kev and 335 Kev γ-rays a level at 1432 Kev has been suggested (Ferguson, 1959). The present observation of a β group of log ft. 5·6 leading to the 1430 Kev state indicates that this level could have a 1/2-, 3/2 or 5/2–assignment. The 70 Kev transition cannot be fitted in the existing decay scheme, so that it should be starting from another level at least 70 Kev above one of the known excited states.

Based on the implications of *j-j* coupling shell model that there can exist geometrical relations among the binding energies and excited states of neighbouring nuclei, Lawson and Uretsky (1957) have predicted a set of levels of spin 3/2, 5/2, 7/2, 9/2 and 11/2 in $_{27}Co^{59}$ which has one proton hole in the closed proton shell of 28 such that their centre of gravity lies at 1332 Kev, the energy of the first excited state (2^+) of $_{28}Ni^{60}$. If the 5/2 and 3/2 states at 1097 Kev and 1289 Kev are considered to be two of the set of levels, then it is not possible to include the 1430 Kev level, which is required to have a 3/2 or 5/2 spin from β-decay, also as a member of this group. However, if the 1430 Kev level has a 1/2 assignment, as suggested by Ferguson (1959), then it is not a member of this set at all.

It would be of interest to establish the character of the 1430 Kev state and the state from which the 70 Kev transition proceeds.

The author is much indebted to Dr. B. V. Thosar for some discussions.

Summary

The β-transition from Fe^{59} leading to the 1430 Kev excited state of Co^{59} is observed. In addition to the γ-rays known to exist, a 70 Kev γ-ray and its corresponding conversion line are observed. Its conversion coefficient of $\alpha^{\text{total}} = 0{\cdot}6 \pm 0{\cdot}45$ requires an angular momentum change of not more than two units.

Note added in proof.—In a publication which appeared much after the submission of this paper* angular correlation of γ-rays support the $\frac{1}{2}$-character of the 1430 Kev state, which may be interpreted as the $p\,\frac{1}{2}$ shell model state. Further the new transition, proposed in this paper appears, from their work

* R. L. Heath and others, *Phys. Rev.*, 1960, **118**, 1082.

to be in coincidence with both 1090 and 1290 Kev γ-rays indicating that this transition proceeds from a 1360 Kev or 1500 Kev level in Co^{59}.

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POTENTIAL CONSTANTS AND CALCULATED THERMODYNAMIC PROPERTIES FOR DIIODOETHYLENE

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I. Introduction

The vibrational spectrum of diiodoethylene has been recorded among others by Miller, Weber and Cleveland (1955). From their experimental results they have proposed some tentative assignments of some of the frequencies. In this paper we have attempted to propose the force constants for diiodoethylene, and compare the experimentally observed frequencies with the calculated ones with a view to check the assignments made by earlier workers.

The heat content, free energy, entropy, and heat capacity were calculated for 12 temperatures from 100–1,000° K for the ideal gaseous state at one atmospheric pressure.

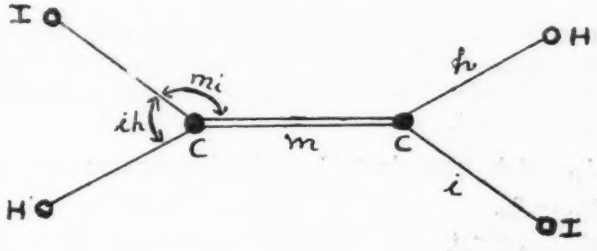
II. Normal Co-ordinate Treatment

The *trans* and the *cis* $C_2H_2I_2$ molecules have 12 normal vibrations the *trans* form having the symmetry of C_{2h} ($5A_g$, $1B_g$, $2A_u$, $4B_u$) point-group and the *cis* that of C_{2v} ($5A_1$, $4B_2$, $2A_2$, $1B_2$) point group. Normal co-ordinate treatments were carried out for both the forms according to Wilson F-G matrix method (1939–40) using the most general quadratic potential energy expression.

The following symbols are used for the equilibrium values of bond distances and interbond angles.

Bond distances.— C—H=h, C—I=i, C=C=m.

Bond angles.— $<$C=C—H=mh, $<$C=C—I=mi, $<$I—C—H=ih.



In accordance with the above notation an example of possible types of the potential constants arising out of various interactions is given below.

f_i = C—I stretching constant.

f_{im} = < I—C=C bending constant.

f_{ih} = < I—C—H bending constant.

f_i^h = C—I and C—H bond-bond interaction constant.

f_i^{hm} = C—I and < C=C—H bond, bending interaction constants.

$f_{ih}{}^{im}$ = < I—C—H and < I—C=C angle-angle interaction constant.

$f_{ih}{}^{-ih}$ = < I—C—H and < I—C—H angle-angle interaction constant across the double bond.

The symmetry co-ordinates for A_g and A_1 types of vibrations are:—

$R_1 = \Delta m.$

$R_2 = 1/\sqrt{2}\,(\Delta i_1 + \Delta i_2).$

$R_3 = 1/\sqrt{2}\,(\Delta h_1 + \Delta h_2).$

$R_4 = 1\sqrt{12}\,(\Delta mi_1 + \Delta mi_2 + \Delta mh_1 + \Delta mh_2 - 2\Delta i_1h_1 - 2\Delta i_2h_2).$

$R_5 = 1/2\,(\Delta mi_1 + \Delta mi_2 - \Delta mh_1 - \Delta mh_2).$

$R_6 = 1/\sqrt{6}\,(\Delta mi_1 + \Delta mi_2 + \Delta mh_1 + \Delta mh_2 + \Delta i_1h_1 + \Delta i_2h_2)$
$\equiv 0$ (Redundant).

The symmetry co-ordinates for B_u and B_1 types are:—

$R_7 = 1/\sqrt{2}\,(\Delta i_1 - \Delta i_2).$

$R_8 = 1/\sqrt{2}\,(\Delta h_1 - \Delta h_2).$

$R_9 = 1/\sqrt{12}\,(\Delta mi_1 - \Delta mi_2 + \Delta mh_1 - \Delta mh_2 - 2\Delta i_1h_1 + 2\Delta i_2h_2).$

$R_{10} = 1/2\,(\Delta mi_1 - \Delta mh_1 - \Delta mi_2 + \Delta mh_2).$

$R_{11} = 1/\sqrt{6}\,(\Delta i_1h_1 - \Delta i_2h_2 + \Delta mi_1 - \Delta mi_2 + \Delta mh_1 - \Delta mh_2)$
$\equiv 0$ (Redundant).

These symmetry co-ordinates are normalised and orthogonal. From the potential energy matrix, *i.e.*, 'f' matrix, and the matrix formed from the coefficients contained in the symmetry co-ordinates the following 'F' matrix elements are obtained.

For A_g and A_1 types the 'F' matrix elements are:—

$F_{11} = f_m.$

$F_{12} = \sqrt{2} f_m{}^{\frac{1}{2}}.$

$F_{13} = \sqrt{2} f_m{}^h.$

$F_{14} = 1/\sqrt{3}\,(f_m{}^{mi} + f_m{}^{mh} - 2f_m{}^{ih}).$

$F_{15} = f_m{}^{mi} - f_m{}^{mh}.$

$F_{22} = f_i + f_i{}^{-i}.$

$F_{23} = f_h{}^i + f_h{}^{-i}.$

$F_{24} = 1/\sqrt{6}\,(f_i{}^{mi} + f_i{}^{-mi} + f_i{}^{mh} + f_i{}^{-mh} - 2f_i{}^{ih} - 2f_i{}^{-ih}).$

$F_{25} = 1/\sqrt{2}\,(f_i{}^{mi} + f_i{}^{-mi} - f_i{}^{mh} - f_i{}^{-mh}).$

$F_{33} = {}_{J}h + f_h{}^{-h}.$

$F_{34} = 1/\sqrt{6}\,(f_h{}^{mi} + f_h{}^{-mi} + f_h{}^{mh} + f_h{}^{-mh} - 2f_h{}^{ih} - 2f_h{}^{-ih}).$

$F_{35} = 1/\sqrt{2}\,(f_h{}^{mi} + f_h{}^{-mi} - f_h{}^{mh} - f_h{}^{-mh}).$

$F_{44} = 1/6\,(4f_{ih} + 4f_{ih}{}^{-ih} + f_{mi} + f_{mh} - 4f_{ih}{}^{mi} - 4f_{ih}{}^{-mi} - 4f_{ih}{}^{mh} - 4f_{ih}{}^{-mh} + f_{mi}{}^{-mi} + f_{mh}{}^{-mh} + 2f_{mi}{}^{mh} + 2f_{mi}{}^{-mh}).$

$F_{45} = 1/\sqrt{12}\,(f_{mi} - f_{mh} + f_{mh}{}^{-mi} - f_{mh}{}^{-mh} - 2f_{ih}{}^{mi} - 2f_{ih}{}^{-mi} + 2f_{ih}{}^{mh} + 2f_{ih}{}^{-mh}).$

$F_{55} = 1/2\,(f_{mi} + f_{mi}{}^{-mi} + f_{mh} + {}_{J}mh^{-mh} - 2f_{mi}{}^{mh} - 2f_{mi}{}^{-mh}).$

For B_u and B_1 vibrations the '**F**' matrix elements are:—

$F_{11} = f_i - f_i{}^{-i}.$

$F_{12} = f_i{}^h - f_i{}^{-h}.$

$F_{13} = 1/\sqrt{6}\,(f_i{}^{mi} - {}_{J}i^{-mi} + f_i{}^{mh} - f_i{}^{-mh} - 2{}_{J}i^{ih} + 2f_i{}^{-ih}).$

$F_{14} = 1/\sqrt{2}\,(f_i{}^{mi} - f_i{}^{-mi} - f_i{}^{mh} + 2f_i{}^{-mh}).$

$F_{22} = f_h - f_h{}^{-h}.$

$F_{23} = 1/\sqrt{6}\,({}_{J}h^{mi} - f_h{}^{-mi} + f_h{}^{mh} + f_h{}^{-mh} - 2f_h{}^{ih} + 2f_h{}^{-ih}).$

$F_{24} = 1/\sqrt{2}\,({}_{J}h^{mi} - f_h{}^{-mi} - f_h{}^{mh} + f_h{}^{-mh}).$

$F_{33} = 1/6\,(f_{mi} - f_{mi}{}^{-mi} + f_{mh} - f_{mh}{}^{-mh} + 4f_{ih} - 4f_{ih}{}^{-ih} - 4f_{mi}{}^{ih} + 4f_{mi}{}^{-ih} - 4f_{mh}{}^{ih} + 4f_{mh}{}^{-ih} + 2f_{mi}{}^{mh} - 2f_{mi}{}^{-mh}).$

$F_{34} = 1/\sqrt{12}\,({}_{J}mi - f_{mi}{}^{-mi} - 2{}_{J}mi^{ih} + 2f_{mi}{}^{-ih} - f_{mh} + f_{mh}{}^{-mh} + 2f_{mh}{}^{ih} - 2f_{mh}{}^{-ih}).$

$F_{44} = 1/2\,(f_{mi} - f_{mi}{}^{-mi} - 2{}_{J}mi^{mh} + 2f_{mi}{}^{-mh} + f_{mh} - f_{mh}{}^{-mh}).$

The elements of the ' G ' matrices* obtained by the Decius Tables (1948 are as follows.

$$G_{11} = 2\mu_c, \quad G_{12} = \sqrt{2}\mu_c \cos mi, \quad G_{13} = \sqrt{2}\mu_c \cos mh,$$
$$G_{14} = -\sqrt{3}\mu_c (\sin mi/i + \sin mh/h),$$
$$G_{15} = -\mu_c (\sin mi/i - \sin mh/h).$$
$$G_{22} = \mu_c + \mu_1, \quad G_{23} = \mu_c \cos ih, \quad G_{24} = (1/2)\mu_c \sqrt{6} (\sin ih/h).$$
$$G_{25} = -\sqrt{2}\mu_c \{(2 \sin mi/m + 1/2 \sin ih/h)\}.$$
$$G_{33} = \mu_c + \mu_H, \quad G_{34} = 1/2\,\mu_c \sqrt{6} \sin ih/i.$$
$$G_{35} = \sqrt{2}\mu_c (2 \sin mh/m + 1/2 \sin ih/i).$$
$$G_{44} = 3/2 \{\mu_1/i^2 + \mu_H/h^2 + \mu_c (1/i^2 + 1/h^2 - 2 \cos ih/ih)\}.$$
$$G_{45} = \sqrt{3}/2 \{\mu_1/i^2 - \mu_H/h^2 + \mu_c (1/i^2 - 1/h^2 - 4 \cos mi/mi + 4 \cos mh/mh)\},$$
$$G_{55} = 1/2 (\mu_H/h^2) + 1/2 (\mu_1/i^2) + \mu_c [(8/m^2) + 1/2 (1/h^2) + 1/2 (1/i^2) - 4 \cos mi/mi - 4 \cos mh/mh + \cos ih/ih)].$$

For B_u vibrations the elements of the ' G ' matrices are:—

$$G_{11} = \mu_c + \mu_1, \quad G_{12} = \mu_c \cos ih, \quad G_{13} = 1/2\,\mu_c \sqrt{6} \sin ih/h,$$
$$G_{14} = -1/\sqrt{2}\,\mu_c \sin ih/h.$$
$$G_{22} = \mu_c + \mu_H, \quad G_{23} = 1/2\,\mu_c \sqrt{6} \sin ih/i, \quad G_{24} = 1/\sqrt{2}\,\mu_c \sin ih/i.$$
$$G_{33} = 3/2 \{(\mu_1/i^2) + (\mu_H/h^2) + \mu_c (1/i^2 + 1/h^2 - 2 \cos ih/ih)\}.$$
$$G_{34} = \sqrt{3}/2 \{(\mu_1/i^2) - (\mu_H/h^2) + \mu_c (1/i^2 - 1/h^2)\}.$$
$$G_{44} = 1/2 \{(\mu_1/i^2) + (\mu_H/h^2) + \mu_c (1/i^2 + 1/h^2 + 2 \cos ih/ih)\}.$$

The elements of the ' G ' matrix for the *cis* form for A_1 and B_1 vibrations:

$G_{ik}^{A_1} = G_{ik}^{A_g}$ and $G_{ik}^{B_1} = G_{ik}^{B_u}$ except for the following;

$G_{25}^{A_1} = G_{14}^{B_u}$, $G_{35}^{A_1} = G_{24}^{B_u}$, $G_{45}^{A_1} = G_{34}^{B_u}$, $G_{55}^{A_1} = G_{44}^{B_u}$

$G_{14}^{B_1} = G_{25}^{A_g}$, $G_{24}^{B_1} = G_{35}^{A_g}$, $G_{34}^{B_1} = G_{45}^{A_g}$ and $G_{44}^{B_1} = G_{55}^{A_g}$.

For calculating the ' G ' matrix elements the values of the bond distances, bond-bond angles and masses of the different atoms are taken from Table I (1955).

The potential constants were transferred from *trans* $C_2H_2Br_2$ (1957) as a first approximation. At first all interaction constants across C=C bond

* The μs in the 'G' matrix elements are the reciprocal of the mass of the atom, the suffix indicating the atom.

TABLE I

Bond distances, interbond angles, moments of inertia and masses of different atoms for cis *and* trans *diiodoethylene*

	Trans $C_2H_2I_2$	*Cis* $C_2H_2I_2$	
Bond distance			Mass of the atom
C—H	1·071 Å	1·071 Å	m_H = 1,008 (a.w.u.)
C—I	2·030 Å	2·030 Å	m_I = 126·9 (a.w.u.)
C=C	1·353 Å	1·353 Å	m_C = 12·01 (a.w.u.)
Interbond angles			Moments of Interia
>C=C—H	120°	120°	$I^t_x = 9{\cdot}972$, $I^t_y = 1537$, $I^t_z = 1547$
>C=C—I	122°	125°	$I^c_x = 874{\cdot}1$, $I^c_y = 72{\cdot}67$, $I^c_z = 874{\cdot}1$

Note.—The symmetry number for both the forms = 2. The moments of inertia are given in units of (a.w.u.A^2).

were set equal to zero. As a consequence of the heavier mass of the iodine atom it was found necessary to reduce the potential constants corresponding to stretching and bond-angle interactions. Introduction of the angle-angle interaction terms across the double bond—$f_{im}{}^{-hm}$, $f_{im}{}^{-im}$, etc.—brought closer agreement between the calculated and the observed values of the vibrational frequencies. After a number of modifications the observed frequencies were reproduced by calculations with an error well within 1% except for ν_5 (A_g). The error for ν_5 is about 5% but the actual difference between the observed and the calculated values is only 8 $cm.^{-1}$

The potential constants thus adjusted for the *trans* molecule were then transferred to *cis* $C_2H_2I_2$. After some modifications mainly in the bond-angle and angle-angle interaction terms it was found necessary to introduce $f_i{}^{-ih}$, $f_i{}^{-hm}$ and $f_i{}^{-im}$ in order to bring about closer fit with the observed values. In the case of the *cis* molecule except for ν_5 (A_1) the observed values were reproduced to well within 1% by calculations. The potential constants thus finally obtained are given in Table II.

The calculated and the observed values of the in-plane vibrational frequencies for both the molecules are given in Table III.

TABLE II

Potential constants for diiodoethylene (cis *and* trans)

Pot. Const.	*Trans*	*Cis*	Pot. Const.	*Trans*	*Cis*
f_h	5·2	5·2	f_h^{-hm}	0·0	0·0
f_i	2·5	2·4	f_h^{im}	−0·04	−0·04
f_m	9·2	9·2	f_h^{-im}	0·0	0·0
f_i^h	0·08	0·08	f_m^{im}	0·08	0·08
f_i^{-h}	0·0	0·0	f_m^{hm}	0·15	0·15
f_i^m	1·0	1·0	f_m^{ih}	−0·04	−0·04
f_h^m	0·05	0·05	f_{ih}	0·4375	0·3531
f_h^{-h}	0·0	0·0	f_{hm}	0·6058	0·6052
f_i^{-i}	0·10	0·0	f_{im}	0·90	0·95
f_i^{ih}	−0·13	−0·2856	f_{ih}^{im}	0·08	0·0675
f_i^{-ih}	0·0	0·0806	f_{ih}^{-im}	0·10	0·0875
f_i^{hm}	−0·20	−0·20	f_{ih}^{hm}	0·08	0·08
f_i^{-hm}	0·0	−0·075	f_{ih}^{-hm}	−0·05	−0·05
f_i^{im}	−0·07	−0·07	f_{im}^{hm}	0·08	0·08
f_i^{-im}	0·0	−0·075	f_{ih}^{-ih}	−0·0625	+0·0219
f_i^{ih}	0·2	0·2	f_{im}^{-hm}	0·10	0·10
f_i^{-ih}	0·0	0·0	f_{im}^{-im}	−0·10	−0·05
f_h^{hm}	0·10	0·10	f_{hm}^{-hm}	0·05	0·05

Note.—Bond constants and bond-bond interaction constants are given in md/A, bond-angle interaction constants in md/rad, and angle constants and angle-angle interaction constants are given in mdA/(rad).[2]

III. THERMODYNAMIC PROPERTIES

The heat content, free energy, entropy and heat capacity at constant pressure for *cis* and *trans* $C_2H_2I_2$ with a rigid rotation, harmonic oscillator approximation for the ideal gaseous state at one atmospheric pressure were calculated for 12 temperatures in 100–1,000° K. range. Since no data were available for the vibrational frequencies in the gaseous state, the values for the liquid state given in Table III are used in the calculations. The results are given in Tables IV and V.

TABLE III

Observed and calculated values of the fundamental frequencies of cis *and* trans $C_2H_2I_2$

Trans $C_2H_2I_2$			*Cis* $C_2H_2I_2$		
Type	Observed	Calculated	Type	Observed	Calculated
A_g ν_1	3,026	3,080	A_1 ν_1	3,030	3,084
,, ν_2	1,537	1,551	,, ν_2	1,545	1,546
,, ν_3	1,225	1,220	,, ν_3	1,120	1,133
,, ν_4	663	666	,, ν_4	495	493
,, ν_5	154	146	,, ν_5	85	63
B_u ν_8	3,069	3,076	B_1 ν_8	3,023	3,075
,, ν_9	1,128	1,140	,, ν_9	1,219	1,219
,, ν_{10}	588	585	,, ν_{10}	672	676
,, ν_{11}	214	215	,, ν_{11}	400	397

Note.—ν_6 and ν_7 are frequencies of the out-of-plane modes. The frequencies are given in cm.$^{-1}$

TABLE IV

Heat content, free energy, entropy and heat capacity for trans $C_2H_2I_2$

T° K.	$(H_\circ - E_\circ^\circ)/T$	$-(F_\circ - E_\circ^\circ)/T$	S°	C_p°
100	9·92	54·43	64·34	12·13
200	11·74	61·87	73·63	14·97
273	12·58	65·40	77·99	16·47
298	13·25	66·86	80·11	17·64
300	13·27	66·94	80·22	17·69
400	14·67	70·95	85·63	19·98
500	15·92	74·37	90·29	21·77
600	17·02	77·37	94·39	23·17
700	17·98	80·07	98·05	24·30
800	18·83	82·52	101·35	25·23
900	19·59	84·79	104·37	26·00
1,000	20·26	86·89	107·15	26·67

TABLE V

Heat content, free energy, entropy and heat capacity for cis $C_2H_2I_2$

T° K.	$(H_o - E_o^\circ)/T$	$-(F_o - E_o^\circ)/T$	S°	C_p°
100	9·45	55·04	64·49	11·23
200	11·18	62·12	73·30	14·67
273	12·11	65·48	77·59	16·46
298	12·86	66·90	79·81	17·75
300	12·89	66·98	79·86	17·85
400	14·43	70·90	85·33	20·19
500	15·77	74·25	90·04	21·98
600	16·92	77·25	94·17	23·36
700	17·92	79·93	97·86	24·45
800	18·80	82·38	101·18	25·36
900	19·57	84·65	104·22	26·12
1,000	20·26	86·75	107·01	26·77

Note.—The temperature is given in K and other quantities are in cal. deg.$^{-1}$ mole^{-1}.

IV. SUMMARY

The *cis* and *trans* diiodoethylenes have been subjected to normal co-ordinate analysis. The Wilson F-G Matrix method has been employed to obtain the secular equation in order to calculate the fundamental frequencies. The potential constants for the 'bromo' molecule were transferred to the molecule under investigation and were so adjusted as to obtain a close fit between the observed and the calculated values of the frequencies. The two low frequencies do not closely agree with the observed values.

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VI. REFERENCES

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